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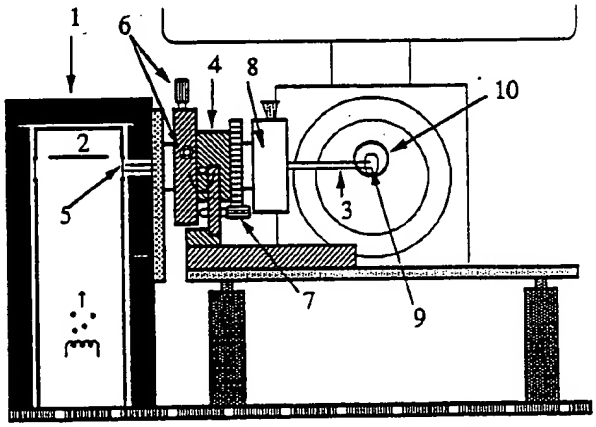
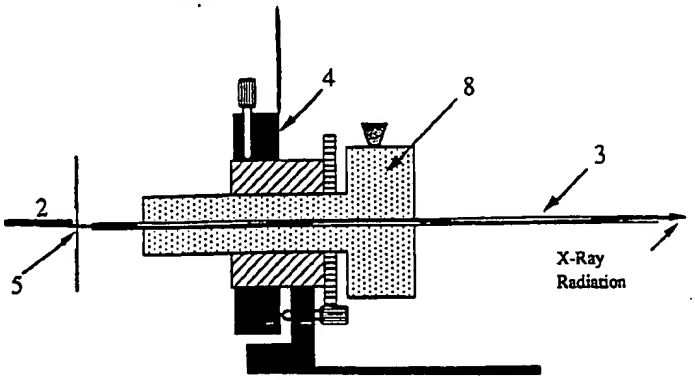
(57) Abstract

The innovation concerns a construction of an instrument for analysis of trace elements in samples with a dimension in the size of mm with the use of X-ray-induced X-ray-fluorescence. The instrument consists of a microbeam of monochromatic X-rays and an X-ray detector (10) for detecting the fluorescent radiation from the sample (9). As X-ray source an X-ray tube (1) is used with a line focus (2) and the radiation is guided out to the sample by a capillary (3). By utilizing the total reflexion of X-rays which can take place inside the capillary (3), high intensity as well as an efficient suppression of high energy X-rays as compared with low energy X-rays, can be achieved. At the same time, by utilizing the selective absorption which occur for low "take off" angles (the angle between the capillary and the anode plane), the radiation both below (lower energy) and above (higher energy) the characteristic radiation from the anode can be effectively suppressed.





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X-ray microbeam spectrometer

Instrument for analysing trace elements in micrometer-sized sample volumes

The innovation concerns an instrument for detecting trace amounts of different elements in sample volumes with a size of its linear dimension down to about one micrometer. The innovation is based on a technique to achieve monochromatic microbeams of X-ray from a conventional X-ray tube by utilizing the selective absorption of X-rays in the anode and the reflecting properties of X-rays inside capillary tubes

X-ray induced X-ray fluorescence has been used for analysing elements since long time. X-ray tubes or radioactive sources has normally been used as X-ray sources. Theses types of X-ray sources are isotropic and microbeams of X-rays can be achieved by collimating the beam with the use of absorbing materials. This means that only a small fraction of the source intensity can be utilized and for beamsizes down to about 100 µm in diameter, only X-ray tubes sources can provide the sufficient intensity for generating any detectable amount of fluorescent radiation.

By using X-ray tubes as the source the sample will be exposed to the characteristic X-ray lines from the anode as well as a continuous distribution of X-rays (the bremsstralungspectra) which will reduce the sensitivity for detecting fluorescent radiation substantially due to the scattering of primary radiation into the detector, which always take place inside the sample. Because of the penetrating power of X-rays and the construction of the X-ray tube, the collimator, used for

generating a small beam, has to be relatively thick and placed a certain distance away from the source, which will reduce the intensity of X-rays out from the collimator.

With the present innovation these problems are removed. By utilizing the total reflexion of X-rays that take place inside glass capillaries, where the surface quality is sufficiently high, a beam intensity can be achieved which would correspond to the intensity achieved with an infinitely thin collimator placed very close to the source. By using the point focal output from a line-focus X-ray tube (the electron beam is focused into a long and narrow line on the anode) very small virtual pointsources can be achieved if the angle between the beam and the anode plane is small. Thus, if the capillary is applied in such a small angle the intensity will be high because almost every point on the focal spot can contribute to the intensity of X-rays inside the capillary. We can now take the advantage of the selective absorption inside the anode which occur for radiation emitted from the anode at these small angles. Due to this absorption the main part of the X-ray radiation, which has an energy lower than the energy of the characteristic X-ray lines from the anode material, can be efficiently suppressed. By utilizing the energy-dependent reflectivety of X-ray inside the capillary the main part of the X-ray radiation, which has an energy higher than the energy of the characteristic X-ray lines from the anode material, can be efficiently suppressed (thus, most of the bremsstralung X-ray is suppressed). This can be done by selecting proper values for the capillary length and diameter and also to select a suitable surface quality of the capillary. As the critical angle for total reflexion of X-rays is very small the beam out from a capillary is almost parallel. By encapsulate the capillary in a vessel filled with mercury, or any other X-ray absorbing material, one can prevent any radiation from penetrating the vessel outside the capillary. To summarize, it is possible to achieve an almost monochromatic and parallel X-ray beam

with a size of a few μm and with an intensity sufficient for analysing trace amounts of different element. As the stray-radiation (radiation outside the main beam) is efficiently suppressed by the absorbing material (mercury e.g) the beam can be used for transmission analysis, microdiffraction or microtomography.

Description of the capillary technique

It is a well known phenomena that X-rays, as well as optical light, can be totally reflected when the photons pass from one medium to another (see U. Ringström Fysik 2b, Almqvist & Wiksell 1970 or R. W. James, The Optical Principles of the Diffraction of X-rays G. Bell and sons LTD London 1962). In difference to the optical light the index of refraction for X-rays in different materials is very close -but below- unity. Thus, total reflexion of X-rays can take place when the X-rays are passing from a "less dense" medium into a "dense" medium. This will only take place for very small angles of incident. Despite this difference it is possible to attain a technique for guiding X-rays through "hollow" fibres (thus capillaries) in analogy with the optical fibre technique. The intensity of X-rays inside the capillary will depend on the critical angle (thus, the largest angle for which total reflexion can occur), and, as this angle is heavily dependent on the X-ray energy, the spectral distribution of the X-rays will be affected when passing through the capillary. For high energies the critical angles are in general small why only a small bundle of X-rays can be collected inside the capillary. As the critical angle is increasing with decreasing X-ray energy larger bundles of these X-rays can be collected inside the capillary. This means that the high energy part of the X-ray spectra will be suppressed in relation to the low energy part while passing the capillary. This suppression can be made very strong if the capillary has a sufficient length. By using a large entrance diameter (the capillary opening close to

the X-ray source) and small output diameter (the capillary opening far from the X-ray source) the high energy X-rays can be further suppressed (this corresponds to conical shaped capillaries below).

Capillaries can be manufactured from many different types of glass materials but only a few of these materials will provide a surface quality sufficient for total reflexion of X-rays. By coating the inside of the capillary with a thin layer of heavy metals (Titanium or heavier) the reflectivety can be increased. For X-ray energies close to any absorption-edge (energies where the absorption of X-rays has a sharp increase) in the surface material the critical angle can attain "extreme" values which can be utilized by combining the anode-material (rather the energy of the characteristic X-ray lines from the anode-material) with the surface-material (rather the energy of the absorption-edge in the surface-material).

Description of the X-ray microbeam spectrometer

The spectrometer, as described in fig. 1, is based on a X-ray tube 1 with a with a line focus 2 on the anode. The capillary, which is attached to a vessel 8 filled with mercury in order to absorb any radiation outside the capillary, is put in close proximity to the beryllium window at the point focal output 5 (in parallel with the line focus) of the X-ray tube. The vessel 8 (with the mercury) together with the capillary constitutes the so called capillary collimator. The vessel is put into a holder 4 which can be adjusted with high precision in a plane perpendicular to the X-ray beam (coming out from the capillary) as well as parallel to it by means of two micrometer screws 6. The tilt-angles in the vertical and horizontal plane of the spectrometer are also adjustable with high precision by two other micrometer screws 7. with these screws the "take off" angle (the angle between the capillary and the anode

plane) can be carefully adjusted which will determined the strength of the selective absorption within the anode.

The X-ray will pass inside the capillary 3 and the sample 9 to be analysed will be applied precisely in front of the capillary output. The fluorescent radiation of characteristic X-rays from the atoms in the sample will be detected by a semiconducting detector 10, which, due to the fact that the beam is very small and parallel, can be placed very close to the sample. This will give a very efficient detection of the fluorescent radiation. Semiconducting detectors for detecting X-rays are usually made of silicon or germanium crystals with a large intrinsic volume and a high voltage is applied over this crystal (see R. Woldseth, X-ray Energy spectrometry Kevex Corp. Burlinggame California U.S.A 1973 or G. Bertolini and G. Restelli, Spectrometry with solid state detectors. Atomic Inner-Shell Processes vol II ed. B. Crasemann Academic Press New York 1975).

By measuring the intensity out from the capillary 3 and at the same time adjusting its position (with the micrometer screws), an optimal position (corresponding to the largest intensity of X-rays) can easily be determined. The largest intensity will normally be attained at very small "take off" angle. At these angles the projection of the focalspot at the plane perpendicular to the beam will be so small that almost every point at the focalspot can contribute to the intensity inside the capillary. At these small "take off" angles the selective absorption in the anode will be so strong that the "bremsstralung" radiation (the non-characteristic part of the X-ray spectra out from the X-ray tube) will be heavily suppressed compared to the characteristic X-ray lines from the anode material. Thus the outgoing X-ray beam from the capillary will be highly monochromatic which will enhance the sensitivity for trace element analysis (see fig. 2).

Fig. 3a and 3b represents spectra from a hair analysis with a chromium- resp. molybdenum-anode in the X-ray tube and with a capillary made of boronsilicate with a diameter of 200 µm.

Application areas

With this innovation, as described above, it will be possible to study the distribution of trace elements in a variety of different samples. By controlling the movement of the sample during the analysis "maps" of the trace element distribution can be generated. we would think that this would be of very great analytical interest within the fields of medicine, geology and also metallurgy. We would like to point out that even the most modern electronmicroscop, equipped with X-ray detectors, in general only can detect elements with a concentration above 0.1%. With the technique, as described above, it will be possible to study trace elements in single biological cells. These types of analysis has previously only been carried out for certain elements and then with the use of proton microbeams. The proton beam can only be generated by big accelerators which are normally only accessible at large national laboratories. With the innovation, as described above, small X-ray microbeam spectrometers can be constructed for these types of analysis and at a relative low cost. It is our opinion that such an instrument would represent a great commercial interest in the whole world.

We claim:

1. An instrument for detecting trace amounts of elements from X-ray induced X-ray fluorescence in samples which can have linear dimensions down to one micrometer, and which is characterized by an X-ray tube (1) with a line focus (2), a capillary collimator, which serves in analogy with the optical fibre technique, and an energy dispersive X-ray detector (10).
2. An instrument according to claim 1, characterized by a microbeam of almost monochromatic X-rays from a X-ray tube (1) with a line focus (2) and an energy dispersive X-ray detector (10).
3. An instrument according to claim 1 and 2, characterized by the fact that the X-ray beam is taken out through a capillary collimator and in an angle between the capillary and the normal to the focal plane which is larger then 85 degrees so that a substantial part of X-rays is absorbed in the anode.
4. An instrument according to claim 1 - 3, characterized by a capillary collimator comprising a capillary (3) encapsulated into vessel (8) filled with mercury.
5. An instrument according to claim 1 - 3, characterized by a capillary collimator comprising a capillary (3) encapsulated into vessel (8) filled with any X-ray absorbing material except mercury, as lead or tungsten or any chemical components of these elements.
6. An instrument according to claim 1 - 5, characterized by a capillary with alength larger than 50 mm and a diameter less then 0.5 mm so that the main part of the radiation inside the capillary will be reflected several times (considerable more than two times) when passing through the capillary.
7. An instrument according to claim 1 - 5, characterized by the fact that the capillary comprise a conical part (entrance diameter larger then the output diameter)

larger than 30 mm and with the largest opening closest to the sources and with a cone angle lower than 0.2 degrees.

8. An instrument according to claim 1 - 5, characterized by the fact that the inside, or part of the inside, of the capillary is covered with a surface layer of some heavy metal in order to influence the spectral distribution of X-rays passing through the capillary.

9. A procedure for trace element analysis with concentrations below 100 ppm (parts per million) characterized by a system comprising an almost monochromatic X-ray microbeam, generated from an X-ray tube (1), with a line focus (2), and a capillary collimator, which serves in analogy with the optical fibre technique, and a energy dispersive X-ray detector (10) for detecting the characteristic X-rays.

Fig 1

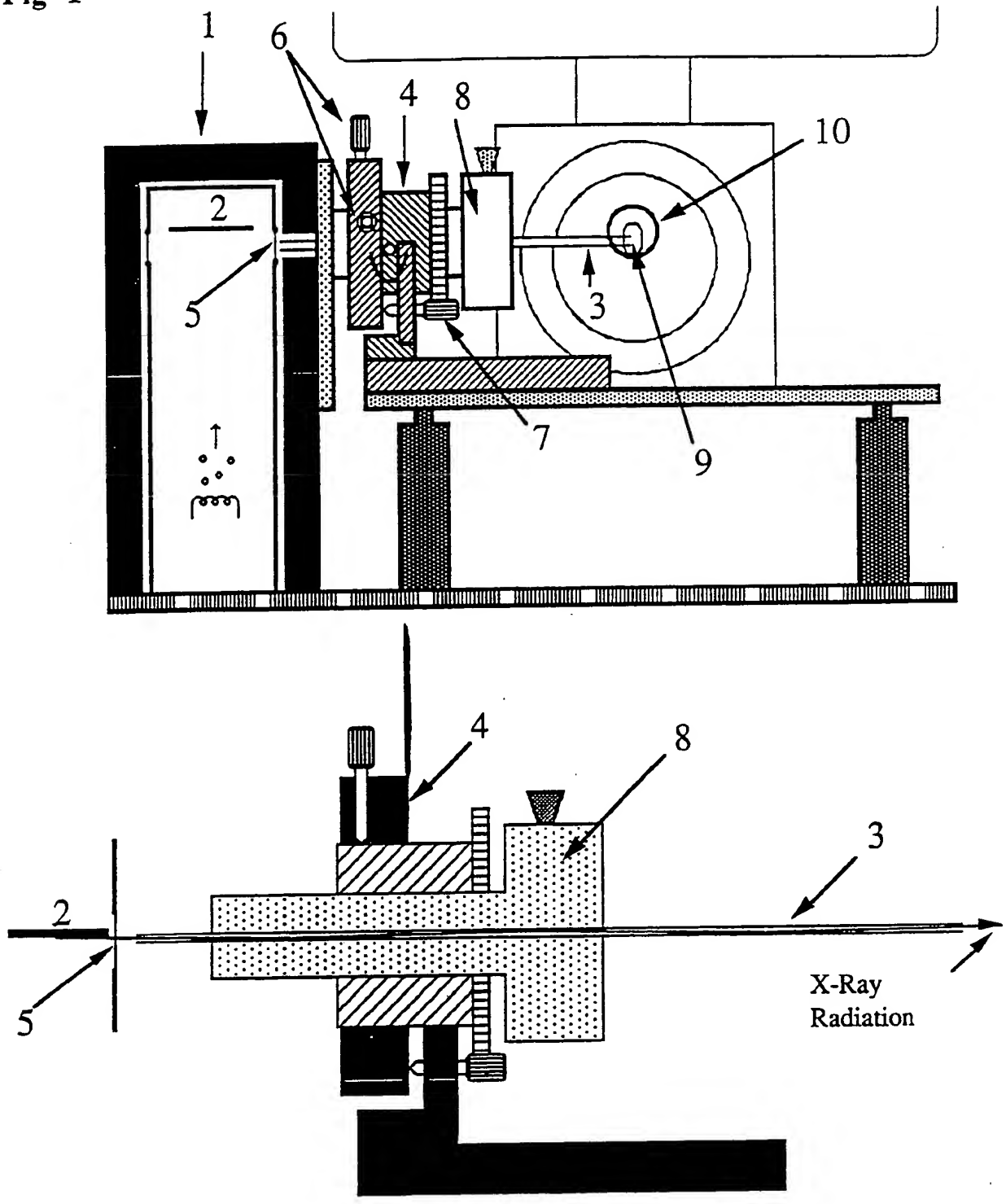

Fig. 1 The spectrometer setup. The lower part shows a crossection of the capillary collimator

Fig 2

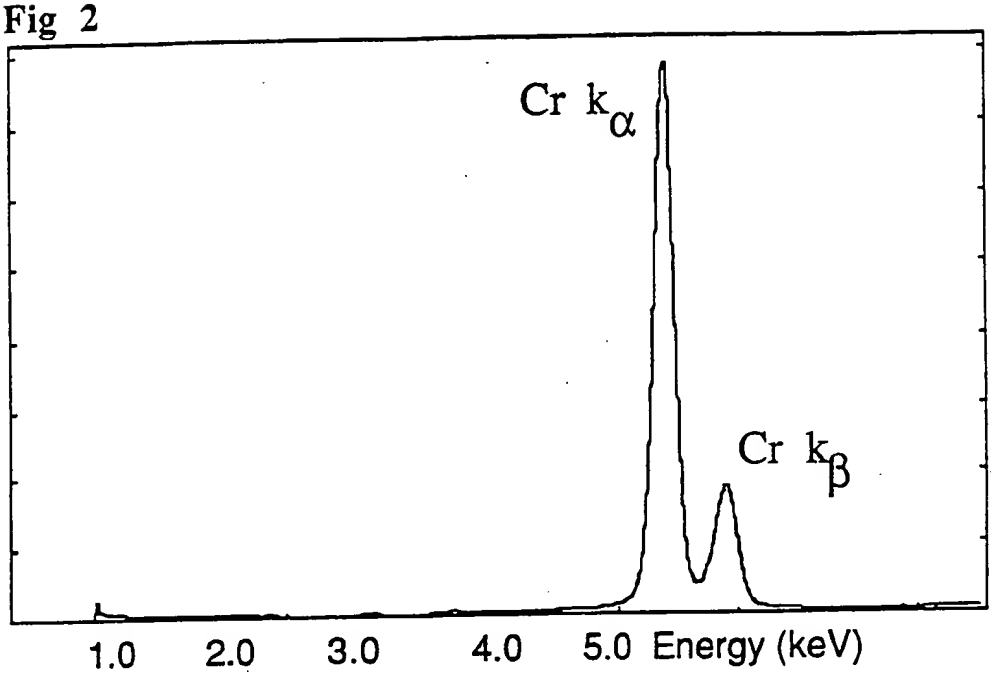

Fig. 2 X-ray spectra from a plexi sample with the Cr tube and a 200 µm capillary

Fig 3a and 3b

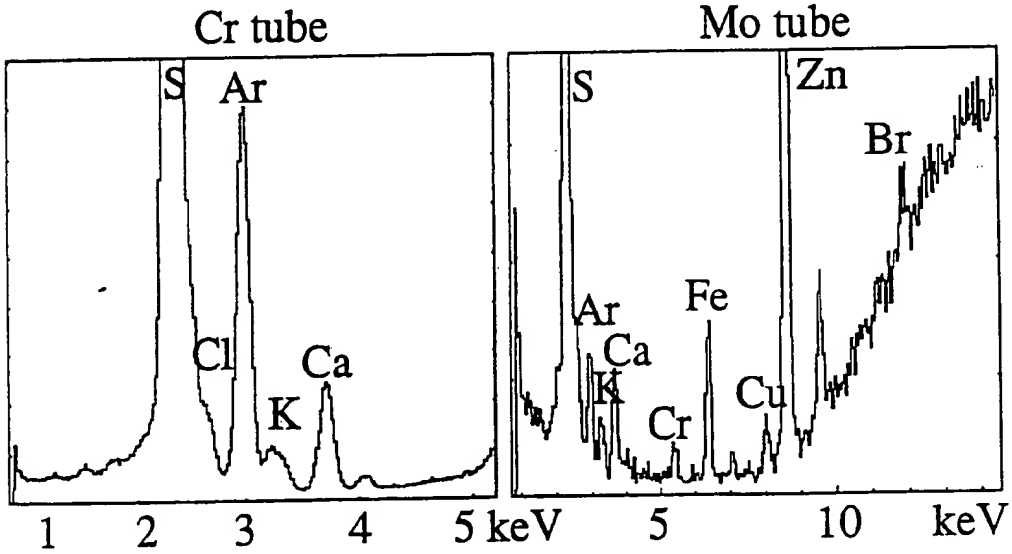

Fig. 3a Spectra from a single hairstrand with Cr anode tube

Fig. 3b Spectra from a single hairstrand with Mo anode tube

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE89/00346

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC 4

G 01 N 23/223

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
IPC 4	G 01 N; G 01 T
US Cl	250; 378

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched *

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	US, A, 4 317 036 (CHIA-GEE WANG) 23 February 1982 see column 5, line 23 – column 6, line 41 and figures 1 and 2	1, 2, 9
Y	Nuclear Instruments and Methods in Physics Research A249 (1986) 536-540, A. Rindby, "APPLICATIONS OF FIBER TECHNIQUE IN THE X-RAY REGION" see page 537 "Apparatus" and "Discussion" page 539	1, 2, 9
P,X	Nuclear Instuments and Methods in Physics Research B36 (1989) 222-226, P Engström et al, "A 200 µm X-RAY MICROBEAM SPECTROMETER"	1-9

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IV. CERTIFICATION

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